

## REDUCING METHYL BROMIDE EMISSIONS FROM FIELDS WITH A SHEET CONTAINING TITANIUM DIOXIDE

**Y. Kobara<sup>a</sup>, Y. Ishii<sup>a</sup>, S. Ishihara<sup>a</sup> and K. Inao<sup>b</sup>**

<sup>a</sup>Laboratory of Environmental Pesticide Assessment, National Institute of Agro-Environmental Sciences, 1-1, Kannondai 3-Chome, Tsukuba, Ibaraki 305-8604, Japan

<sup>b</sup>Agricultural Chemicals Inspection Station  
2-772, Suzuki-cho, Kodaira, Tokyo 187-0011, Japan

Methyl Bromide (CH<sub>3</sub>Br) is a major fumigant used in Japan to control soil-borne diseases in crops such as cucumbers, gingers, tomatoes, melons, green peppers, etc. The use of CH<sub>3</sub>Br as a soil fumigant is to be phased out by 2005, but no new chemical or non-chemical alternative has yet emerged as its substitute. For now, 1,3-dichloropropene and chloropicrin are seen as the best alternatives to CH<sub>3</sub>Br for preplant fumigation, and their sales are increasing steadily. They are considered risky and unsuitable as long-term replacements. It is difficult to adequately satisfy demand for CH<sub>3</sub>Br as a soil fumigant, as only some critical use exemptions and emergency use are permitted now.

Restrictions on CH<sub>3</sub>Br usage have led to an intensive search for improved technologies to reduce both dosage and emission from fumigated plots into the atmosphere, while maintaining its effectiveness for disease and weed control. Various kinds of improved field management practices have been shown to limit CH<sub>3</sub>Br emission in several countries. These methods can reduce the amount of CH<sub>3</sub>Br application and its emission during exposure period. However, such techniques are not entirely suitable in Japanese conditions.

The standard dose of CH<sub>3</sub>Br application in Japan varies from 15 to 30 g m<sup>-2</sup>, which is near threshold level, and it is difficult to reduce the dosage dramatically by using a gas-tight film alone. In previous studies, we found that using a multilayer sheet containing titanium dioxide in surface application considerably reduced emission loss to some % of the applied amount, which consisted of 3 layers: an impermeable layer, a photocatalyst layer and a support layer from top to bottom. TiO<sub>2</sub> photo-semiconductor helps in degradation of CH<sub>3</sub>Br to carbon dioxide (CO<sub>2</sub>), hydrogen bromide (HBr) and water. Decomposition and removal rates of CH<sub>3</sub>Br by this sheet are strongly dependent on solar radiation. However, soil fumigation by CH<sub>3</sub>Br is done in all seasons in Japanese horticulture. The purpose of this study is to develop and evaluate a new multi-layer sheet for use in surface application of CH<sub>3</sub>Br in different seasons. We presumed that emission could be reduced significantly if CH<sub>3</sub>Br degradation is enhanced by a photocatalyst in all seasons, although this approach has not yet been well investigated.

This technique was evaluated in field experiments from 5 to 30 May (Trial 1), from 26 August to 20 September (Trial 2), 16 November to 5 December in 1998 (Trial 3), and 4 to 20 August in 1999 (Trial 4) on Hydric Hapludand soils at the National Institute of Agro-Environmental Sciences, Tsukuba, Japan. "Cold gas method" was used for fumigation by releasing CH<sub>3</sub>Br (32.8 g m<sup>-2</sup>) from cans onto the soil surface (15 m<sup>2</sup>) under a sheet, which was removed after 7 or 9 d. An automated gas chromatography system, equipped with flame ionization detectors (GC-FID) and four 7.5 L chambers

(diam. 24.5 cm) was used to determine emission flux. The chambers were placed directly on the sheet or soil surface. Concentrations of  $\text{CH}_3\text{Br}$  in the air below the film and at soil depths of 30, 60, 90, 120, 150 cm were measured. Two detectors were used for measuring gas concentrations: the Brüel & Kjær 1301 FT-IR-photoacoustic spectrometer for  $\text{CH}_3\text{Br}$ ,  $\text{CO}_2$ , and water vapor, and the gas chromatograph for  $\text{CH}_3\text{Br}$ .

$\text{CH}_3\text{Br}$  concentration at the beginning of the experiment was over 15,000 ppm. Although decomposition and removal rates of  $\text{CH}_3\text{Br}$  are slow and dependent on solar radiation,  $\text{CH}_3\text{Br}$  concentration below the sheet declined rapidly during the period of covering in the field (7 or 9 d). Although the solar radiation and ambient temperature varied widely in each experiment, just before the removal of the sheet,  $\text{CH}_3\text{Br}$  concentration between the sheet and soil surface decreased to a few ppm with the multi-layer sheet in all experiments, as against over 1,000 ppm with a gas-tight film. As  $\text{HBr}$  generated was neutralized immediately by the soil in field conditions, most  $\text{CH}_3\text{Br}$  recovered in the field at the end of the experiment was near the soil surface and the sheet. Our experiments also showed that  $\text{CH}_3\text{Br}$  emission was reduced to less than some % of the applied amount by using the sheet containing  $\text{TiO}_2$ . Moreover,  $\text{CH}_3\text{Br}$  concentrations below the multi-layer sheet and gas-tight film were largely similar until the middle of fumigation period. This indicates that under field conditions, the use of multi-layer sheet may not greatly reduce the efficacy of  $\text{CH}_3\text{Br}$  fumigation.

The multi-layer sheet can be used easily and repeatedly without any major modifications in current practice of soil surface application. Further, the problem in disposing this sheet is minimal. We, therefore, believe that the technique is useful for reducing  $\text{CH}_3\text{Br}$  emissions substantially and holds promise for commercial use. Simultaneously, however, we must study ways to improve methods of application of various chemical alternatives to  $\text{CH}_3\text{Br}$ .